

Self-Diffusion in Wormlike Micelles Networks with Electrostatic Interactions: A Universal Behavior?

Janaky Narayanan,^{1,*} W. Urbach,^{1,†} D. Langevin,¹ C. Manohar,² and R. Zana³

¹Laboratoire de Physique Statistique de l'E.N.S., 24 Rue Lhomond, 75231, Paris Cedex 05, France

²Chemistry Division, Bhabha Atomic Research Centre, Bombay 400 085, India

³Institut Charles Sadron (CRM-CNRS), 6 Rue Boussingault, 67083, Strasbourg Cedex, France

(Received 26 November 1997)

We report measurements of the self-diffusion coefficient of several wormlike micellar solutions in the semidilute regime. We show that the existing “living polymer” models can account for the results only if the effect of electrostatics on the micellar growth is taken into account. The behavior of the different systems is remarkably similar, and this is due to the fact that the micelles scission energies are relatively system independent. [S0031-9007(98)06505-3]

PACS numbers: 82.70.-y, 36.20.-r, 61.25.Hq, 66.10.Cb

When dissolved in water, surfactant molecules can self-assemble and form aggregates such as spherical micelles, bilayers, or other varied structures [1]. In dilute solutions, the type of aggregate is determined by the interactions between surfactant molecules: For charged, single chain surfactants, the electrostatic repulsion between the polar parts of the molecules is stronger than the effective steric repulsion between the chains due to packing constraints, and spherical micelles are formed; with double chain surfactants, the steric repulsion between chains almost balances the electrostatic repulsion, and flat bilayers are usually formed. Intermediate cylindrical shapes were also predicted to exist [1], and were observed later on with a variety of single chain cationic surfactants in the presence of added salts [2]. The length of the cylindrical micelles increases with surfactant concentration due to the progressive screening of the electrostatic repulsions by the surfactant electrical charges, and these micelles can become very long (contour lengths of microns). Their persistence length being of the order of 10 nm, they have wormlike shapes like flexible polymer chains; as polymers, they entangle above an overlap concentration c^* , and the solutions become viscoelastic. In contrast to polymer chains, the micelles can break and recombine, and their average length depends upon their concentration. Quite remarkably, theoretical treatments by Cates and co-workers [3] allow us to describe quantitatively the rheological behavior of the solutions. They have motivated a large number of studies on wormlike micelles, which have, from the practical point of view, many interesting applications (drag reduction, etc.) [4].

In semidilute polymer solutions ($c > c^*$), the elastic modulus is controlled by the number of chain entanglements; the viscosity and the self-diffusion of the polymer chains depends on the reptation time, time taken by a chain to disentangle from its neighbors and renew its environment [5]. Wormlike micelles break and recombine with a characteristic time τ_{break} ; the frequency behavior of the viscoelasticity is similar to that of polymers above frequencies ω of order τ_{break}^{-1} , but very different be-

low $\omega < \tau_{\text{break}}^{-1}$. Self-diffusion can be conveniently studied with fluorescent probes dissolved in the micelles. At time scales longer than τ_{break} , the self-diffusion coefficient of the micelles is predicted to scale with the surfactant concentration as $D \sim c^{-\alpha}$ with an exponent α different than for polymers (for which $\alpha = 2$) because of the scission events [6]. Theory predicts α values ranging from 1.3 to 1.7 according to the type of scission process [7]. Power laws of the type $D \sim c^{-\alpha}$ were indeed found above $c > c^*$ in all of the systems that were studied in the presence of excess added salt, i.e., when the electrostatic interactions are entirely screened (Debye length smaller than the distance between surfactant molecules in the micelles). However, in salt-free systems or in systems where the amount of salt is not sufficient to fully screen the electrostatic interactions, the experimental results are not in accordance with these predictions [8–10]: $\alpha \sim 6$ in salt-free systems. Moreover, in some systems, D goes through a minimum at a higher concentration c^{**} , after which it increases with c , a behavior not correlated with that of the bulk viscosity [9]. In order to clarify these issues, we have undertaken a study of a new type of surfactants, which form wormlike micelles in the absence of added salt. These are “gemini” surfactants, made of two single chain cationic surfactants connected by a spacer at the heads level. In the present paper, we compare the data obtained with these surfactants and those from our earlier studies. We show that the self-diffusion coefficient behavior is universal, provided it is scaled in concentration with c^* . The scaling curve is in excellent agreement with theoretical predictions by Mackintosh *et al.* taking into account the effect of the electrostatic interactions on the micellar growth [11]. An increase of D above c^{**} is also observed with the gemini surfactants, but in this case it is associated with a viscosity maxima.

Gemini surfactants are dimeric cationic surfactants: alkanediyl- α - ω -bis (dimethyl alkylammonium bromide), referred to as m - s - m surfactants (m and s being the carbon numbers of the side alkyl chains and of the alkanediyl spacer, respectively). We have selected for this study

the compounds 12-2-12, 12-3-12, and 16-4-16 which are known to form wormlike micelles [12]. The preparation, purification, and characterization of these dimeric surfactants have been reported elsewhere [13]. The technique of fluorescence recovery after fringe pattern photobleaching (FRAPP) was used to measure the self-diffusion coefficient of fluorescent probes incorporated into the micelles. More details on the technique and on the experimental setup can be found in Refs. [8] and [14].

The measured diffusion coefficients for the gemini surfactants used in this study are shown in Fig. 1. The accuracy on D values is typically better than 4%. We take for c^* the value of the concentration beyond which D decreases drastically: for 12-3-12, $c^* \sim 0.05$ g/g, and for 12-2-12 and 16-4-16, showing much more rapid growth than 12-3-12 micelles, $c^* \sim 0.02$ g/g. These trends are in line with previous micelle aggregation number measurements and cryotransmission electron microscopy observations which show that the tendency to micelle growth increases when the size of the spacer decreases, and when the chain length increases [15]. The value of c^{**} beyond which D increases with c is found to be 0.15 g/g for 12-3-12 and 0.06 g/g for 12-2-12 and 16-4-16.

Figure 2 shows the normalized D versus c data in units of D_0 (value of D for $c \rightarrow 0$) and c^* , respectively. In this figure, we have also gathered the data on cetylpyridinium chlorate (CPClO₃) [9] and cetyltrimethylammonium tosylate (CTAT) [10] from our previous studies, including new data on CTAT for concentrations above c^{**} (= 0.02 g/g). All the curves nicely collapse together, and a universal behavior is observed both in the dilute and semidilute regimes. This phenomenon can be explained by the following theoretical considerations.

In the Cates model [6], the diffusion coefficient of the micelles in the semidilute regime is given by $D = D_{\text{rep}}(\tau_{\text{break}}/\tau_{\text{rep}})^{-1/3}$, where τ_{rep} is the reptation time of

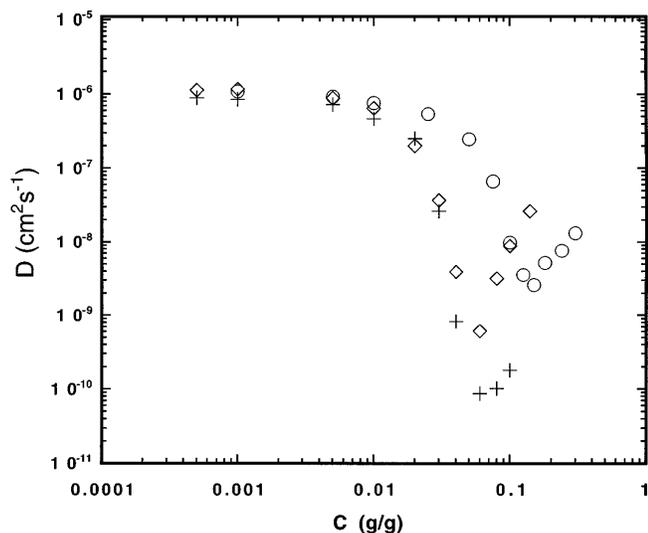


FIG. 1. Variation of D with c for the dimeric surfactants, 12-3-12 at 30 °C (circles), 12-2-12 at 35 °C (diamonds), and 16-4-16 at 35 °C (crosses).

an hypothetical unbreakable micelle of average length L , τ_{break} is the average time before such a micelle breaks into two pieces due to reversible scission process, and D_{rep} is the diffusion coefficient in the limit $\tau_{\text{break}} > \tau_{\text{rep}}$. The average micelle length is given by

$$L \sim c^{1/2} \exp(E/2kT), \quad (1)$$

where E is the scission energy of the micelle. From the polymer theory, one has $D_{\text{rep}} \sim L/\tau_{\text{rep}}$ and $\tau_{\text{rep}} \sim L^3 c^2$ [5]. Assuming $\tau_{\text{break}} \sim 1/L$, we get $D \sim L^{-2/3} c^{-4/3}$, which becomes with Eq. (1): $D \sim c^{-5/3} \sim c^{-1.7}$. This scaling law has been modified by Turner *et al.* [7] by taking into account other scission processes: the end-interchange process (fusion process of two chains forming a three-armed star and subsequent separation into two chains by exchanging segments) and the bond-interchange process (fusion process of two chains to form a four-armed star and subsequent separation into two chains by exchanging segments). The exponent values obtained for these three different kinetic processes range from 1.3 to 1.7. The above models do not take into account the effect of charges on the micelles.

The scission energy E of charged micelles contains, in addition to the end-cap energy E_c that favors the growth of the micelles, an electrostatic contribution E_e that favors the breaking of micelles. In the Mackintosh *et al.* model [11], the electrostatic energy is proportional to the range

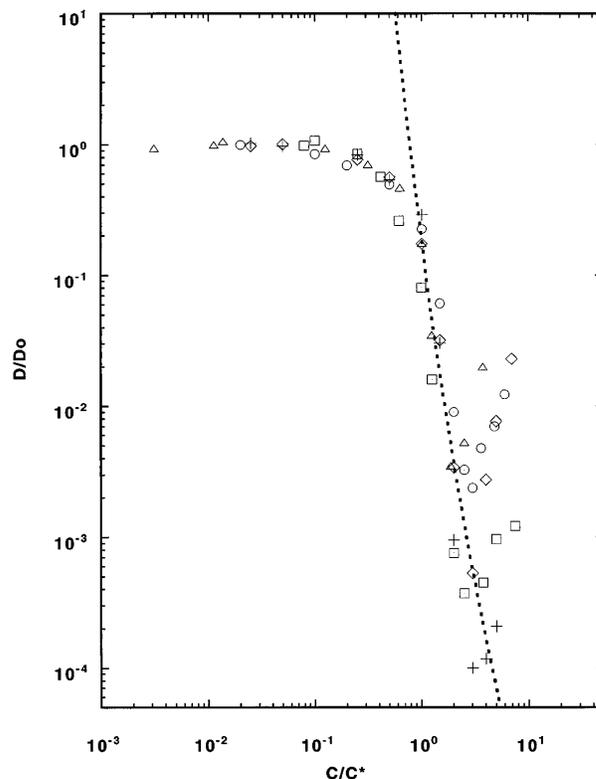


FIG. 2. D/D_0 vs c/c^* for different salt-free surfactants: 12-2-12 at 35 °C (diamonds), 12-3-12 at 30 °C (circles), 16-4-16 at 35 °C (crosses), CTAT at 24.5 °C (squares), and CPClO₃ at 35 °C (triangles). The dotted line is calculated from Eq. (4) with $E_c = 33kT$ in the semidilute regime.

of the electrostatic interactions, i.e., to $c^{-1/2}$ and balances E_c at the overlap concentration. The average micellar length in the semidilute regime is given by

$$L \sim 2c^{1/2} \exp\{(E_c/2kT)[1 - (c^*/c)^{1/2}]\}, \quad (2)$$

where the overlap concentration is

$$c^* \sim (kTl_B a v^*/E_c)^2, \quad (3)$$

with l_B being the Bjerrum length, a is the radius of the cylindrical micelle, and v^* is the effective charge per unit length on the micelle [11]. Substituting Eq. (2) into $D \sim L^{-2/3} c^{-4/3}$ we get

$$D \sim D_0 c^{-5/3} \exp\{(-E_c/3kT)[1 - (c^*/c)^{1/2}]\}. \quad (4)$$

Using the experimental values of c^* and D^* (value of D at c^*), Eq. (4) can be used to fit the data in the semidilute regime with E_c as the fitting parameter. The results of such fits on the salt-free ionic systems are given in Table I. The fits are found to agree well with the data in the semidilute regime ($c^* < c < c^{**}$). The uncertainty on c^* is about 20%, and the corresponding uncertainty on E_c is about 15%. In view of the close values found for E_c only the theoretical curve corresponding to $E_c = 33kT$ is shown for clarity on Fig. 2. Equation (4) explains the behavior of D in the semidilute regime better than any scaling law found in literature. It has to be mentioned here that using a similar argument, Candau and co-workers have explained the behavior of viscosity in several salt-free systems [16]. The values of the effective charge per unit length on the micelle v^* are also listed in Table I, as obtained from the values of c^* by using Eq. (3). It must be stressed that these v^* values are only rough estimates: There could be a prefactor in Eq. (3), c^* is not known accurately, and the radius of the micelles has been approximated by the extended hydrocarbon chain length. One sees in the table that the charge is smaller for CTAT than for CPClO₃, although the area per surfactant molecule at the surface of the micelle is similar. This means that the degree of counterion binding is more important for CTAT. This explains why the micellar growth is much more rapid in CTAT than in CPClO₃ as revealed by the different values of c^* (see Table I). The fact that E_c is similar in the different systems studied

TABLE I. Values of the crossover concentration c^* , the end-cap energy E_c [obtained after fitting diffusion data with Eq. (6)], the charge per unit length of the micelle v^* , and the exponent β (from $D \sim c^\beta$ in the concentrated regime) for different salt-free micellar solutions. v^* was calculated from Eq. (5) with $l_B = 0.7$ nm, $a = 2$ nm for 12-*s*-12 ($s = 2, 3$), and $a = 2.5$ nm for other surfactants.

| Surfactant | t (°C) | c^* (wt %) | E_c/kT | β | v^* |
|--------------------|----------|--------------|----------|---------|-------|
| 12-2-12 | 30 | 0.02 | 30 | 4.4 | 0.17 |
| 12-2-12 | 35 | 0.02 | 33 | 4.4 | 0.18 |
| 12-3-12 | 30 | 0.05 | 30 | 2.2 | 0.22 |
| 16-4-16 | 35 | 0.02 | 31 | 2.2 | 0.16 |
| CTAT | 24.5 | 0.008 | 38 | 2.2 | 0.14 |
| CPClO ₃ | 35 | 0.08 | 34 | 2.2 | 0.23 |

explains the observed universal behavior. E_c represents the difference in surfactant free energy for spherical and cylindrical geometries and is only a small fraction of the micellization energy: about kT per molecule in the micellar end caps. E_c should slightly increase with surfactant chain length and decrease if the head becomes larger. E_c can also be determined from rheological studies and for 12-2-12 Kern *et al.* [17] reported values ranging from $30kT$ to $50kT$. There are no published data for other salt-free systems, but E_c was found to be of the order of $(20-30)kT$ in systems with added salt [3]. The fact that the E_c values are similar for the single chain surfactants might be due to the fact that E_c depends mainly on the chain and that all of the single chain surfactants studied here have 16 carbon atom chains. This would explain why giant micelles are not observed with shorter chains (smaller E_c and limited growth) or longer ones because of insolubility. The current anionic surfactants with C₁₆ chains are insoluble, and no giant micelles are obtained with smaller chain compounds. In the case of nonionic surfactants, giant micelles were obtained with a compound having again a C₁₆ chain and never reported for smaller chains [18].

So far, we have assumed that the micelles are wormlike. However, because of the electrostatic repulsions, the persistence length of these micelles could be larger than for micelles with excess salt, of the order of 15–20 nm [19]. In salt-free systems, the electron micrographs show indeed that the persistence length seems larger: 30–50 nm [15]. For $c^* = 2\%$, the center to center distance of the micelles is of the order of 30 nm, i.e., close to this persistence length. The micelle length increases very rapidly above c^* , so its shape evolves from rod to wormlike very rapidly. It can also be noted that the self-diffusion coefficient of rodlike micelles varies as $D \sim L^{-1}$ [20], which according to Eq. (2) gives $D \sim c^{-1/2} \exp\{(-E_c/2kT)[1 - (c^*/c)^{1/2}]\}$. Because of the exponential term, the variation with c is hardly distinguishable from that of Eq. (4). The numerical factor in the exponential is changed by $\frac{2}{3}$, which would change only the E_c values.

When excess salt is added, the electrostatic interactions are screened and c^* moves to very low values. In such cases, Eq. (4) becomes $D \sim c^{-\alpha}$ and one observes the power law behavior predicted by Turner *et al.* [7]. Unlike most other monomeric surfactants such as CTAB (cetyl trimethyl ammonium bromide), CTAT, and CPClO₃ [8–10], 12-2-12 is found to become rapidly insoluble in the presence of salt. We found that 0.05M is the highest KBr concentration that can be used at 35 °C without phase separation in the system. Figure 3 gives the FRAPP results on 12-2-12 in the presence of 0.02M and 0.05M KBr at 35 °C. Right from the lowest concentration used in this study, we observe the semidilute regime with $D \sim c^{-1.18}$ for 0.02M and $D \sim c^{-0.88}$ for 0.05M salinities. These exponents are smaller than the values derived by Turner *et al.* [7] for reptative diffusion. They are compatible with

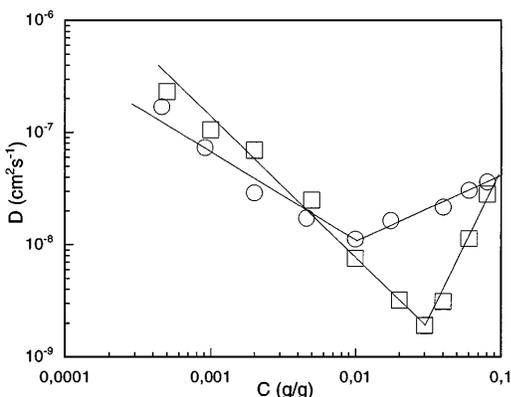


FIG. 3. D vs c for 12-2-12 at 35 °C in the presence of 0.02M KBr (squares) and 0.05M (circles).

diffusion in the “breathing” regime (Rouse fluctuations of the tube formed by the entanglements) [7], but it may be fortuitous. In Fig. 3, no dilute regime is observed as for CPClO₃ + NaClO₃ [9] and CTAT + KBr [10] for salinities higher than 0.1M. In all of the systems studied, the exponent α decreases when the salt concentration increases [8–10], and the α values extracted for high salt concentrations are close to those predicted by the authors of Ref. [7], showing that the diffusion mechanism depends on salt concentration.

Let us now consider the concentrated regime $c > c^{**}$ where D is found to increase with c as $D \sim c^\beta$. In CTAB and CPClO₃ systems, the rheological properties do not show changes in behavior above c^{**} . This led us to assume that the diffusion regime of the fluorescent probe was changing [9]. Indeed, at c^{**} , the motion of the micelles in which the probe is embedded is very slow and the motion of the probe along the micelle can become faster. In such a case, the probe moves along the micelle, then waits until a break arises, and after the recombination, the probe continues its motion on the newly formed micelle. The diffusion coefficient is then predicted to increase with surfactant concentration with a power law exponent β depending again on the type of scission process: β ranges between 0.8 and 1.8, the largest value corresponding to the bond interchange scission. These results are compatible with the measured exponents β (which are around two), except for 12-2-12 for which $\beta \sim 4$ (Table I). Here, the accuracy on β is about 10%. In Ref. [9], the rheological behavior of the studied system was found incompatible with the diffusion model, the possible role of progressive micelle branching above c^{**} was invoked to explain the increase of D with c . In principle, this should be accompanied by a decrease of the viscosity [21], which is indeed observed for 12-2-12 at these concentrations.

In conclusion, we have observed a universal behavior of the self-diffusion coefficient in the semidilute regime of several salt-free micellar solutions. This result can be explained by the Cates model for living polymers, when the effect of electrostatics on the micellar growth is taken into account. The universal behavior is due to the fact

that the micelle scission energy is remarkably similar in the different systems, about $30kT$. In the presence of excess salt, the power laws predicted by Turner *et al.* [7] are obeyed in the semidilute regime, but the exponent is salt dependent and a nonuniversal behavior is observed in this case. The scaling behavior in the concentrated regime where the self-diffusion coefficient increases with the surfactant concentration might be associated with topological changes in these systems.

This work was performed under Project No. 1007-1 of the Indo-French Centre for the Promotion of Advanced Research. J.N. thanks Amir Maldonado and Nicolas Taulier for their help.

*Permanent address: Department of Physics, R.J. College, Bombay 400 086, India.

†To whom correspondence should be addressed.

- [1] J. Israelachvili, D.J. Mitchell, and B.W. Ninham, *J. Chem. Soc. Faraday Trans. 2* **72**, 1525 (1976).
- [2] G. Porte, J. Appell, and Y. Poggi, *J. Phys. Chem.* **84**, 3105 (1980); H. Hoffmann, *Adv. Colloid Interface Sci.* **32**, 123 (1990).
- [3] M.E. Cates and S.J. Candau, *J. Phys. Condens. Matter* **2**, 6869 (1990); R. Granek and M.E. Cates, *J. Chem. Phys.* **96**, 4758 (1992).
- [4] H. Hoffmann, P. Stern, and L. Myska, *Rheol. Acta.* **33**, 419 (1994).
- [5] P.G. de Gennes, *Scaling Concepts in Polymer Physics* (Cornell University, Ithaca, 1979).
- [6] M.E. Cates, *Macromolecules* **20**, 2289 (1987); *J. Phys. (Paris)* **49**, 1593 (1988).
- [7] M.S. Turner, C. Marques, and M.E. Cates, *Langmuir* **9**, 695 (1993).
- [8] R. Messenger, A. Ott, D. Chatenay, W. Urbach, and D. Langevin, *Phys. Rev. Lett.* **60**, 1410 (1988).
- [9] N. Morie, W. Urbach, and D. Langevin, *Phys. Rev. E* **51**, 2150 (1995).
- [10] J. Narayanan, C. Manohar, D. Langevin, and W. Urbach, *Langmuir* **13**, 398 (1997).
- [11] F. Mackintosh, S. Safran, and P. Pincus, *Europhys. Lett.* **12**, 697 (1990).
- [12] R. Zana, *Curr. Opin. Colloid Interface Sci.* **1**, 566 (1996), and references therein.
- [13] R. Zana, M. Benraou, and R. Rueff, *Langmuir* **7**, 1072 (1991).
- [14] J. Davoust, P. Devaux, and L. Leger, *EMBO J.* **1**, 1233 (1982).
- [15] D. Danino, Y. Talmon, and R. Zana, *Langmuir* **11**, 1448 (1995).
- [16] J. Narayanan, C. Manohar, F. Kern, F. Lequeux, and S.J. Candau, *Langmuir* **13**, 5235 (1997).
- [17] F. Kern, F. Lequeux, R. Zana, and S.J. Candau, *Langmuir* **10**, 1714 (1994).
- [18] Z. Lin, L.E. Scriven, and H.T. Davis, *Langmuir* **8**, 2200 (1992).
- [19] J. Appell, G. Porte, and Y. Poggi, *J. Colloid Interface Sci.* **87**, 492 (1982).
- [20] M.E. Cates, C.M. Marquès, and J.P. Bouchaud, *J. Chem. Phys.* **94**, 8529 (1991).
- [21] F. Lequeux, *Europhys. Lett.* **19**, 675 (1992).